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1. Summary

This report summarizes research results during the first part of Phase I of our subcontract, which began in July 2002. The major technical results consist of identification of the conditions for successful silicon epitaxial growth by hot wire CVD on large-grained polycrystalline templates. Epitaxial growth is possible under hydrogen-diluted silane growth conditions in the temperature range 300-400 ^{o}C. Films up to 1 μm were grown, and it was found that films remain crystalline but a multiply twinned film microstructure develops for silicon thickness greater than 250 nm.

2. HWCVD Epitaxial Si Growth on Si (100)

Hot-wire chemical vapor deposition has been shown to be a promising method for fast, low-temperature (<600°C) epitaxy [1, 2]. During the current portion of Phase I, we have investigated low-temperature epitaxial growth of thin silicon films by HWCVD on polycrystalline template layers formed by selective nucleation and solid phase epitaxy (SNSPE). Previously, we showed that direct deposition by HWCVD on SiO_2 produced small grains (~40-80 nm), even with the addition of H_2 to a diluted mixture of 1% silane in He [3]. By varying the gas flow rates and wire-to-substrate distance, we can now grow up to 1 μm thick epitaxial layers at 300ºC on silicon [100] substrates using an H_2:SiH_4 ratio of 70:1. Transmission electron microscopy confirms that the films are epitaxial with a periodic array of stacking faults. SNSPE layers formed by the use of nickel nanoparticles as nucleation sites for the solid-phase crystallization of phosphorus-doped amorphous silicon on SiO_2 display grain sizes on the order of 100 μm, and have been successfully used as seed layers for epitaxial growth by molecular beam epitaxy at 600ºC [4,5]. In this report, we describe the microstructural properties of epitaxial films grown on silicon (001) 'control' substrates and SNSPE templates on glass.

Silicon films of 300 nm thickness were grown on silicon (100) substrates, amorphous silicon dioxide substrates and SNSPE templates by HWCVD using hydrogen and diluted silane in He at an H_2:SiH_4 ratio of 70:1 at a total gas pressure of 170 mTorr. A tungsten filament of 0.5 mm diameter was heated to 1850°C and placed 5 cm from the substrates. These conditions were chosen to produce amorphous silicon films on SiO_2, similar to those investigated by Seitz et al. [2]. Growth temperatures of 300°C − 450°C were chosen to investigate the effect of different levels of hydrogen surface passivation on the resulting epitaxial films. Substrates were UV ozone cleaned for 10 minutes and HF-dipped, then heated to 200°C in vacuum to desorb hydrocarbons. Ultrahigh purity gas mixtures were used and the base pressure of the growth chamber was below 10^{-6} Torr.

Cross-sectional transmission electron microscopy of films grown on silicon (100) substrates at 300°C confirms the presence of epitaxial growth, as shown in Figure 1. The rough film-substrate interface is believed to have been caused by etching of the surface during growth by atomic hydrogen produced by the wire [3]. The roughened appearance of the silicon substrate in cross-section may be due to the presence of hydrogen platelet defects arising from the diffusion of hydrogen into the film during growth, although the exact structure of the defects has yet to be determined. Epitaxy continues to a thickness of approximately 240 nm, after which the film becomes highly twinned. The epitaxial films exhibit a periodic array of stacking faults which gives rise to the higher-order spots seen in the diffraction pattern in Figure 2.

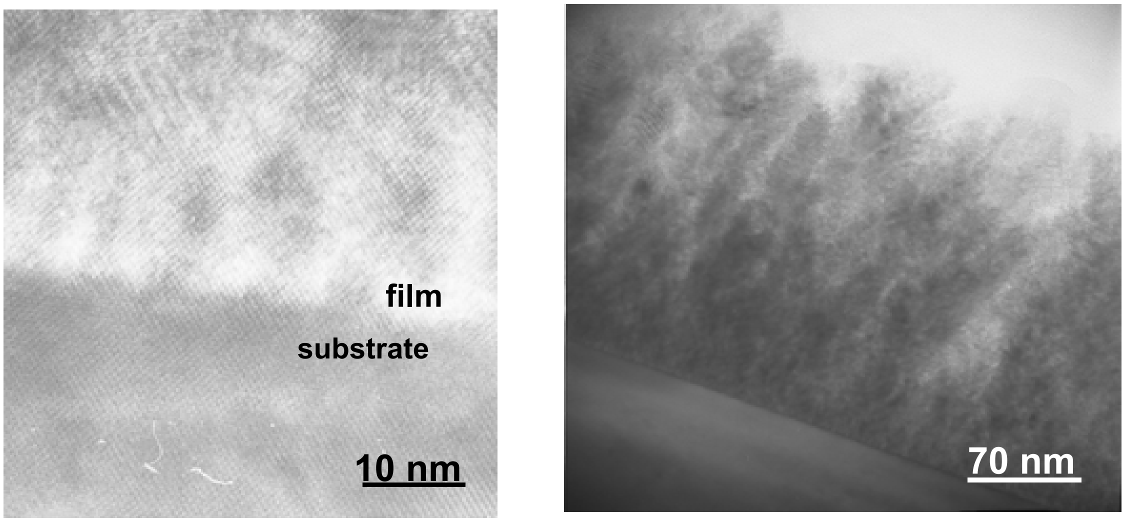

Figure 1. Cross-sectional TEM of Si on Si (100) at 300°C. (a) Interface between Si (100) and HWCVD epitaxial film. (b) Films become highly twinned after a thickness of approximately 240 nm.

The results reported here for hydrogen-diluted epitaxial growth on Si (100) are broadly consistent with work reported elsewhere. Thiesen et al. had previously observed epitaxial growth at temperatures between 195 and 325°C in which stacking fault defects were observed [1], while Seitz and Schröder observed no stacking faults or surface roughening in their epitaxial films grown between 280 and 360°C [2]. Both experiments were done using approximately 10 mTorr of pure SiH_4 and no additional hydrogen. Although Thiesen et al. postulate that low-temperature epitaxy by HWCVD is possible because the growth species is believed to be SiH_3, we believe that for our diluted silane conditions the dominant growth species are silicon atoms [3]. It is possible that low-temperature epitaxial growth under these high hydrogen dilution conditions may be enabled by the preferential etching of amorphous regions by atomic hydrogen from the wire [6].

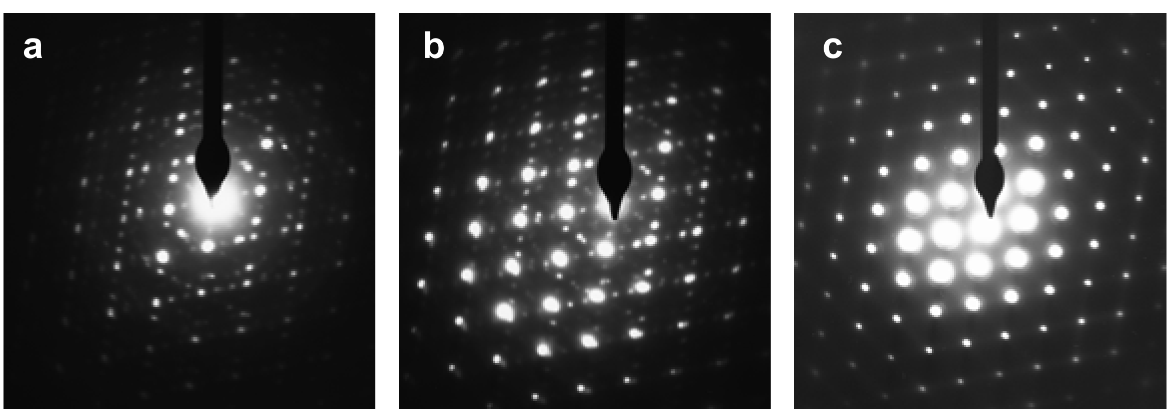

Figure 2. Selected area diffraction patterns. (a) HWCVD film and amorphous glue layer. (b) HWCVD film and Si (100) substrate. (c) Si (100) substrate. Higher order spots in (a) and (b) are due to a periodic array of stacking faults in the epitaxial film and twinning in the uppermost regions of the film.

Silicon films 300 nm thick films on SNSPE templates were investigated through plan-view transmission electron microscopy. The results, seen in Figures 3 and 4, are consistent with low-temperature epitaxy on the scale of the 100 μm grains of the SNSPE templates. Epitaxial breakdown is observed in the diffraction pattern of the HWCVD film, but some of the underlying higher-order diffraction spots are visible, making it likely that the underlying film has a morphology similar to that observed in the HWCVD films on Si (100). The effect of the orientation of the underlying grain structure of the SNSPE template on the morphology of the HWCVD film can be seen in Figure 4.

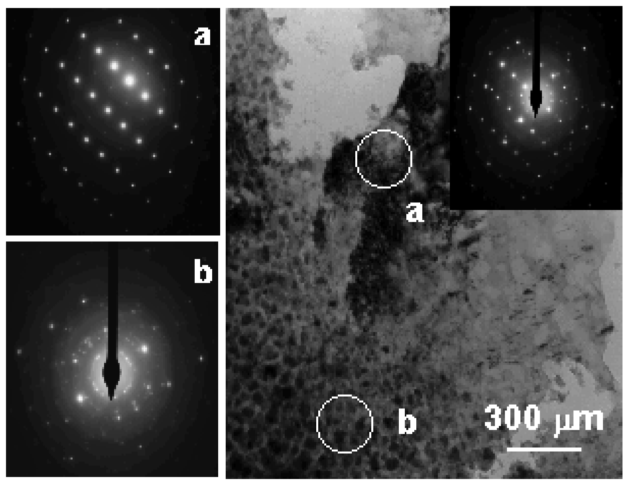

Figure 3. Plan-view TEM of HWCVD epitaxial film (T=300°C) on SNSPE template. (a) Selected area diffraction pattern from underlying SNSPE template. (b) Selected area diffraction pattern from HWCVD film on SNSPE template. (c) Bright-field image indicating selected area diffraction regions. Inset: diffraction from entire area.

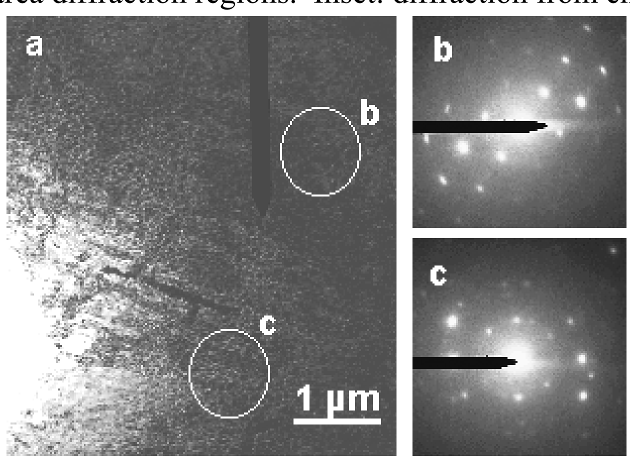

Figure 4. (a) Bright-field image of HWCVD film (T=300°C) on SNSPE template showing selected area diffraction regions. (b) HWCVD film on (100)-oriented grain. (c) HWCVD film on grain of different orientation.

Cross-sectional analysis of these films reveals some areas of epitaxial growth as well as some areas of columnar growth. Before HWCVD growth, the SNSPE templates were cleaned in a solution of 3:7 HNO_3:H_2O, which has been shown by Auger spectroscopy to remove elemental nickel from the template surface [5]. The lack of epitaxy in some areas is thus more likely to have been caused by the presence of ordinary surface contaminants, such as carbon and oxygen. These may be able to be removed by cleaning the surface for a short time with atomic hydrogen from the wire before growth. The SNSPE template layers have been successfully used as seed layers for epitaxy by MBE at 600ºC [4]. It may be shown that a growth temperature of 300ºC is not sufficiently high for epitaxial growth on the template layers; however, we anticipate that by increasing the growth temperature in the range from 300 to 600ºC, epitaxial growth may be achieved with HWCVD with a microstructure consistent with that achieved by MBE.

Epitaxial films characterized by a periodic array of stacking faults have been grown at high hydrogen dilution by HWCVD on Si (100) substrates. The limiting thickness for epitaxy is shown to be approximately 240 nm at a growth temperature of 300ºC, after which the films are highly twinned. Evidence has been presented for epitaxial growth on SNSPE templates with 100 μm grains, although surface contamination may have resulted in columnar growth in some areas. Epitaxial growth on these templates could lead to the development of large-grained thin-film polycrystalline photovoltaic devices. Future work includes efforts toward increased growth rates (currently only 0.15 Å/s) and evaluation of the minority carrier lifetimes of the SNSPE templates and resulting epitaxial films to determine their suitability for photovoltaic applications.

5. References

[1] J. Thiesen, E. Iwaniczko, K.M. Jones, A.H. Mahan, R. Crandall, Appl. Phys. Lett. 75 (1999).

[2] H. Seitz, B. Schröder, Sol. State Comm. 116 (2000).

[3] J.K. Holt, M. Swiatek, D.G. Goodwin, R.P. Muller, W.A. Goddard III, H.A. Atwater, Thin Solid Films 395 (2001).

[4] C.M. Chen, Ph.D. Thesis, California Institute of Technology, 2001.

[5] R.A. Puglisi, H. Tanabe, C.M. Chen, H.A. Atwater, Mat. Sci. Eng. B 73 (2000).

[6] H.N. Wanka, M.B. Schubert, Mat. Res. Soc. Symp. Proc

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